Thermodynamics of cement degradation

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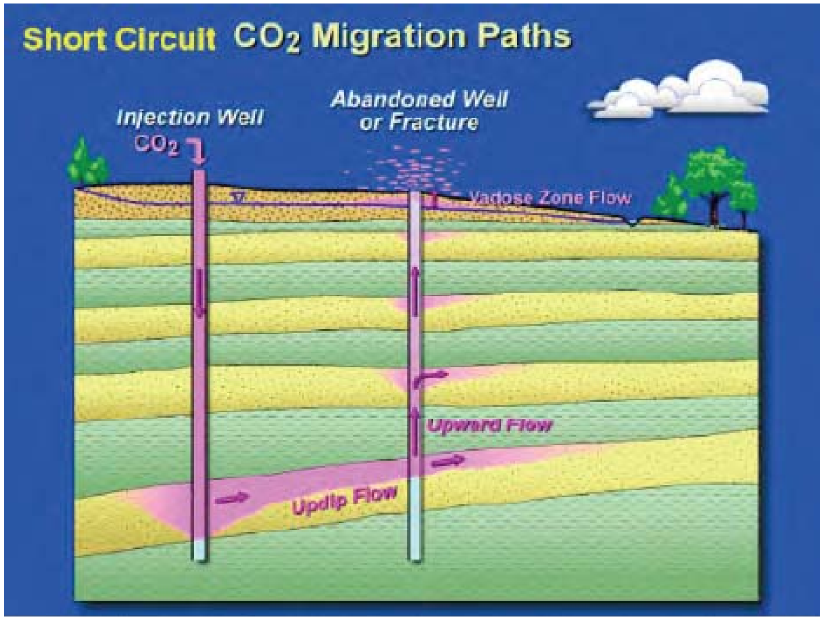
- **Introduction:**
- **A. Thermodynamic properties of cement hydrates**
  - ✓ C-S-H, AFm, AFt, Hydrogarnets: what do we know and what can we estimate?
- **B. What can we learn from a logK data set and how?**
  - ✓ Reactions path modeling as a first step into analyzing a thermodynamic dataset
- **C. Towards quantitative long term predictions…**
  - ✓ Use of dedicated reactive/transport model: specificity of cement pastes
- **Conclusion:**

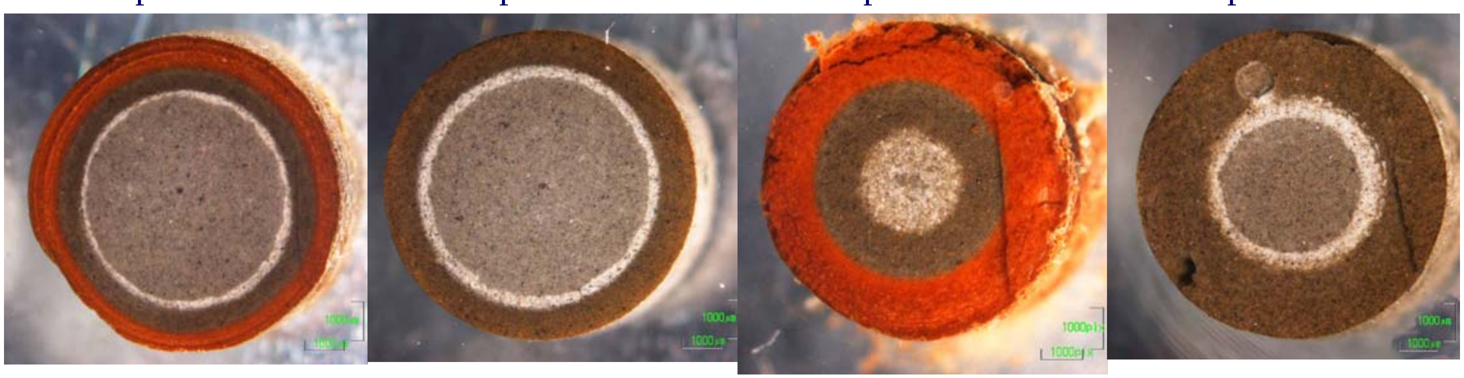
✓ CO2 storage in deep saline aquifers



From Canadian CO2 Capture and Storage Roadmap Strawdog, Bill Gunter, Alberta Research Council

✓ Duguid's experiment of cement degradation in CO_2 saturated brine (after 31 days)

Neat paste 23°C pH 2.4	Neat paste 23°C pH 3.7	Neat paste 50°C pH 2.4	Neat paste 50°C pH 3.7



A. Thermodynamic properties of cement hydrates

What data/model are required ?

√ **Activity correction model (Debye Huckel, B-dot,..)**

√ **Thermodynamic properties of Aqueous species:**

⇨ **nature of the aqueous complex and their LogK**

SUPCRT'92 (LLNL)

× **Thermodynamic properties of cement phases:**

- o **C-S-H**
- o **AFt / AFm**
- o **Hydrogarnets**

$$\Delta_f G^0_{T_r,P_r}\ ,\quad S^0_{T_r}\ ,\quad C^0_{P_r}(a,b,c),\quad V^0_{T_r,P_r}\quad ?$$

What is the equation of state for minerals ?

-

$$\Delta G^0_{P,T} \quad = \quad \Delta_f G^0 - S^0_{P_r,T_r}(T - Tr) + \int_{T_r}^{T} C^0_{P_r}\, dT - T\int_{T_r}^{T} C^0_{P_r}\, d\ln T + \int_{P_r}^{P} V^0_T\, dP$$

$$C^0_{P_r} \quad = \quad a + bT + cT^{-2}$$

Are the data available in the literature ?

1. Gibbs free energies at 25 °C known for most phases but

- scatter in the results

- erroneous Data/interpretation

- internal consistency of the database

2. Entropies and heat capacities:

- known for only a few cement phases (Babushkin 1985)

3. Molar volumes:

- estimated from lattice parameters and molar mass

Can we handle incomplete set of data ?

1. Asumption $\Delta_r H^0 = cst$ ⇒ Van't Hoff equation

$$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta_r H^0}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

2. Evaluate best estimates of entropy and heat capacity (Helgeson 1979)

use the property of a structural analog

C-S-H: Discrete modeling of the solid solution: LogK = f(Ca/SI)

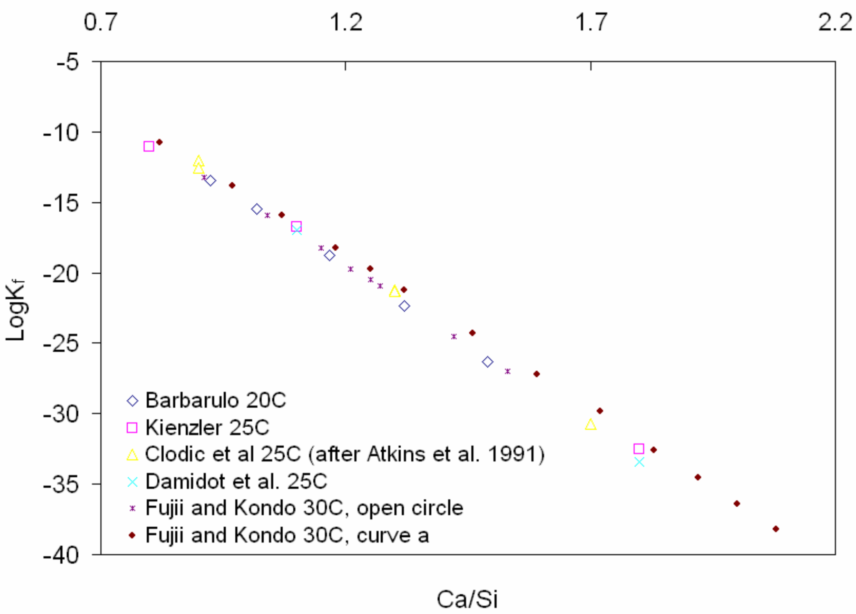
1. **$\Delta_f G^0$** Numerous study, mostly at 25°C
   Linear relationship between LogKf and Ca/Si

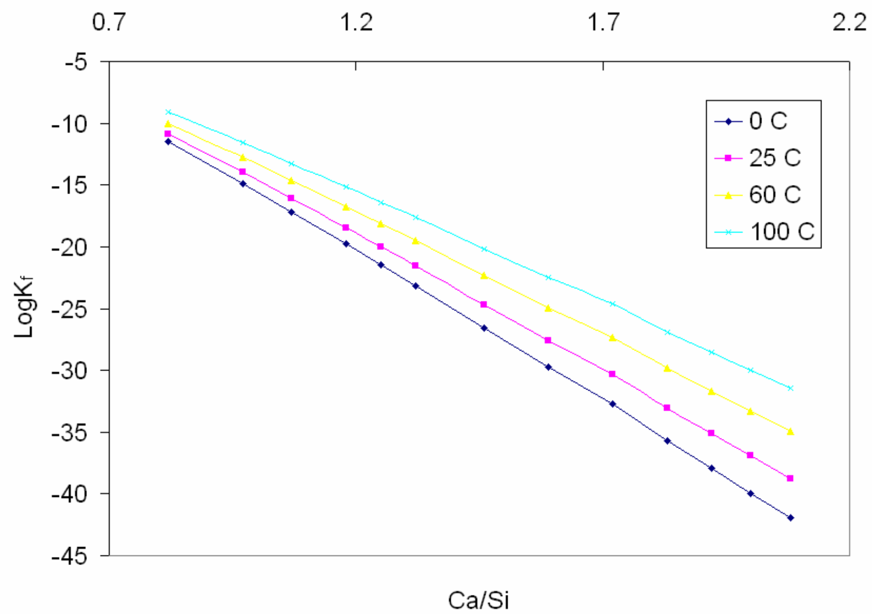
2. **Entropy** and **heat capacity**:

$$6xCaO.SiO_2.(x+0.8)H_2O \Leftrightarrow 5CaO.6SiO_2.5.5H_20+(6x-5)Ca(OH)_2+4.3H_2O$$

3. **Molar volume**:
   density weakly related to Ca/Si: C-S-H(I) 2250 kg.m^3, C-S-H(II) 2350 kg.m^3

4. **Results:**





AFm: Substituion of OH^-, CO_3^{2-}, SO_4^{2-} or Cl^-

1. **$\Delta_f G^0$** available at 25°C
   Complete data set for Calcium monosulfoaluminate

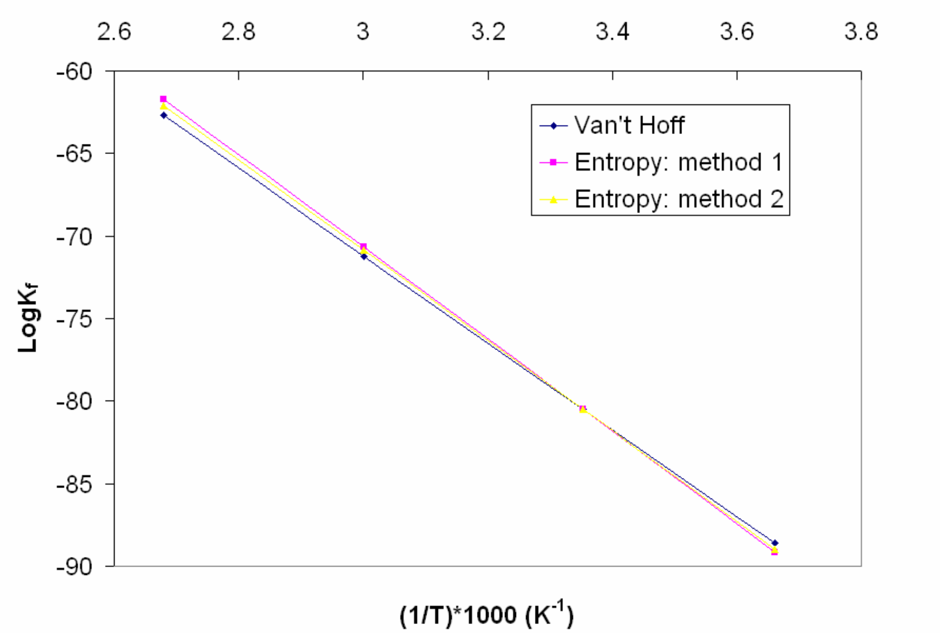
2. **Entropy** and **heat capacity**:

$$3CaO.Al_2O_3.CaCO_3.11H_2O + CaSO_4 + 1\,H_2O_{(z)} \Leftrightarrow 3CaO.Al_2O_3.CaSO_4.12H_2O + CaCO_3$$

....

3. **Molar volume**:
   density or lattice parameter available

4. **Results: example of calcium monocarboaluminate**



AFt: Substituion of CO_3^{2-}, SO_4^{2-} or Cl^-

1. $\Delta_f G^0$ available at 25°C
   Complete data set for ettringite (Babushkin or Perkins and Palmer)

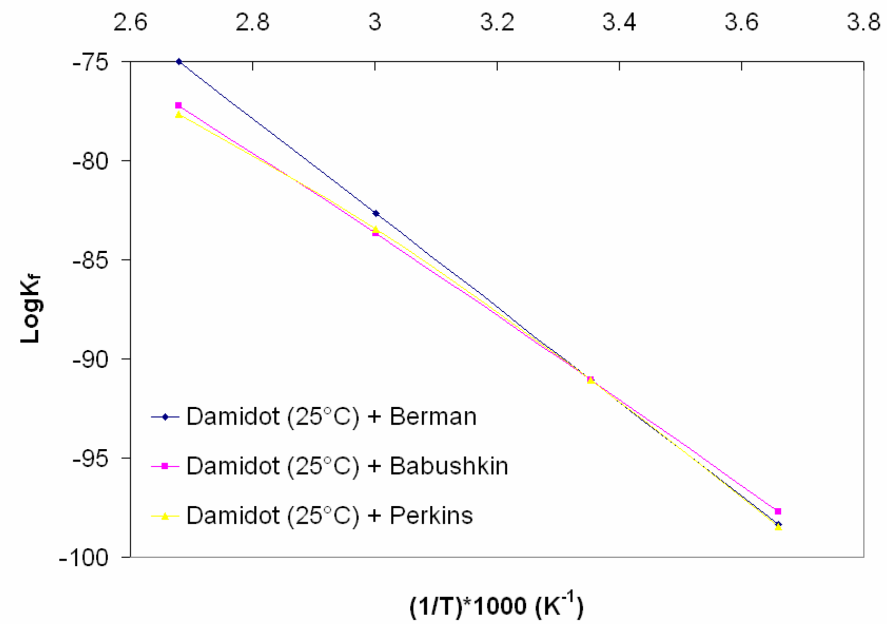
2. **Entropy** and **heat capacity**:

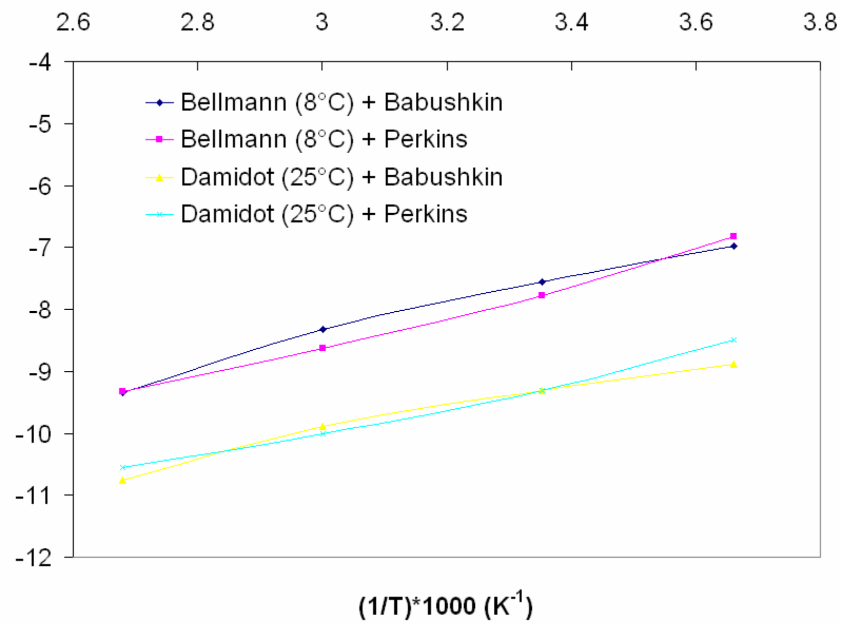
$$3CaO.Al_2O_3.3CaCO_3.32H_2O + 3CaSO_4 \Leftrightarrow 3CaO.Al_2O_3.3CaSO_4.32H_2O + 3CaCO_3$$

....

3. **Molar volume**:
   density or lattice parameter available

4. **Results**: calcium tricarboaluminate and thaumasite





B. What can we learn from a logK data set and how ?

Aim :

1- Study the change of the chemical composition of a given cement with T or any extensive variables .

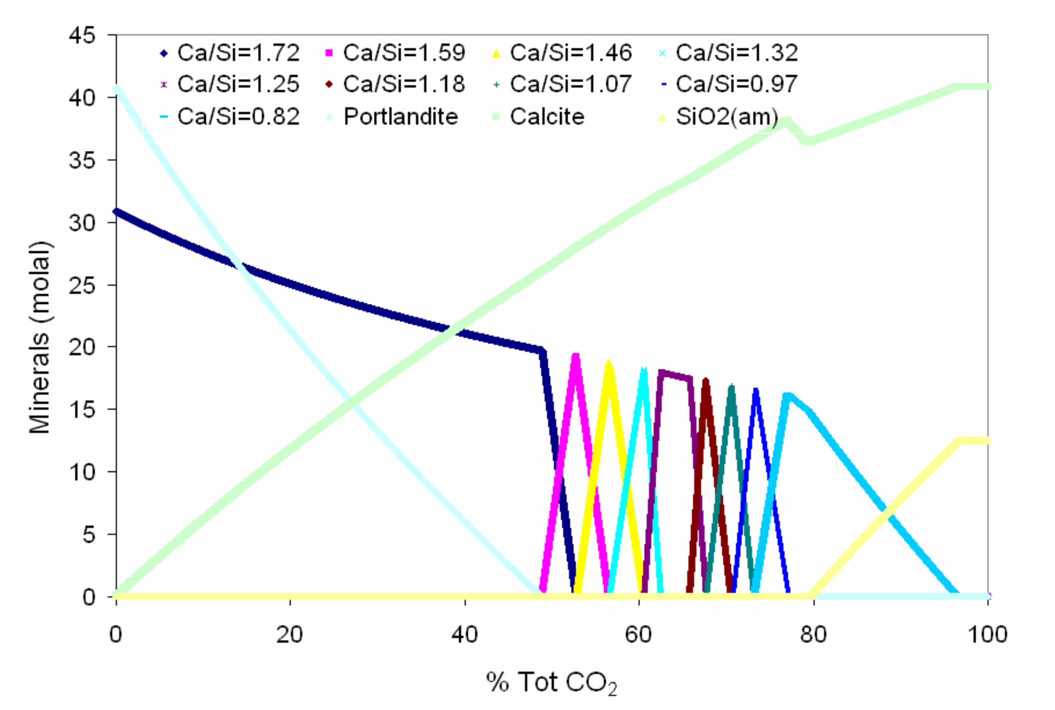
2-Make the LogK database useful for the engineer using simpler tool than reactive transport code.

Method:

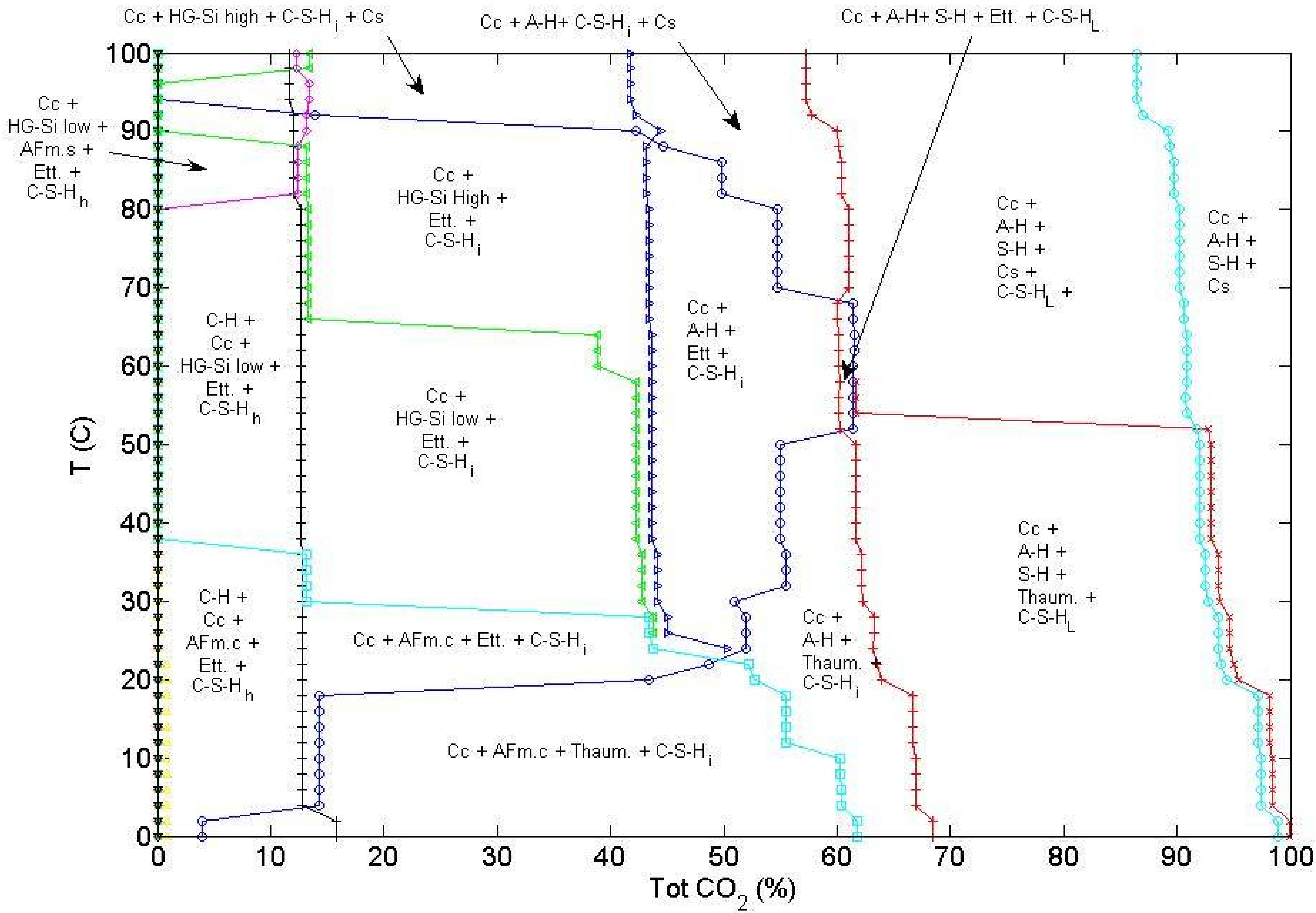
Use of geochemical reaction path model

Exemple:

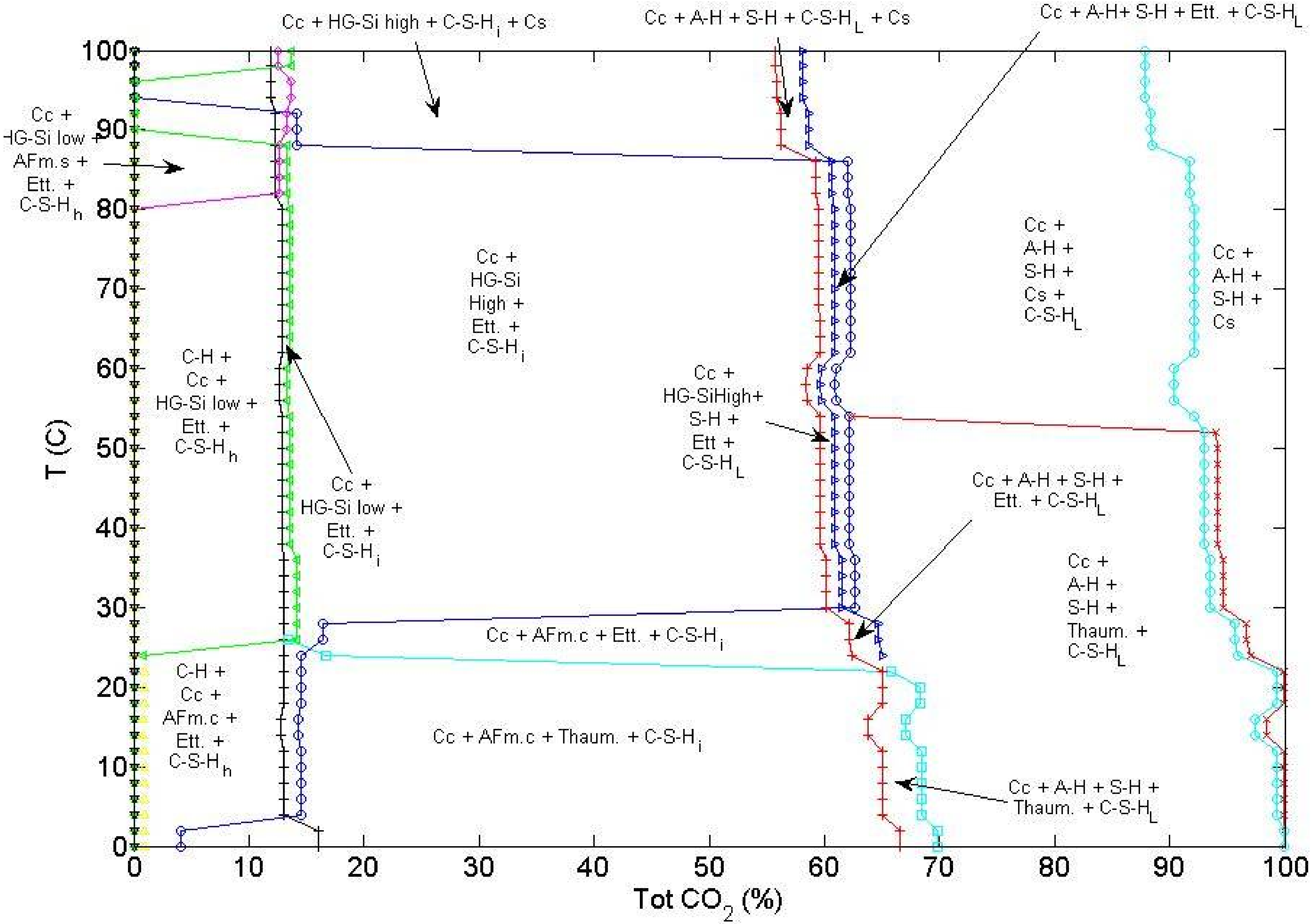
Addition of CO_2 in a fully hydrated cement paste (closed system)



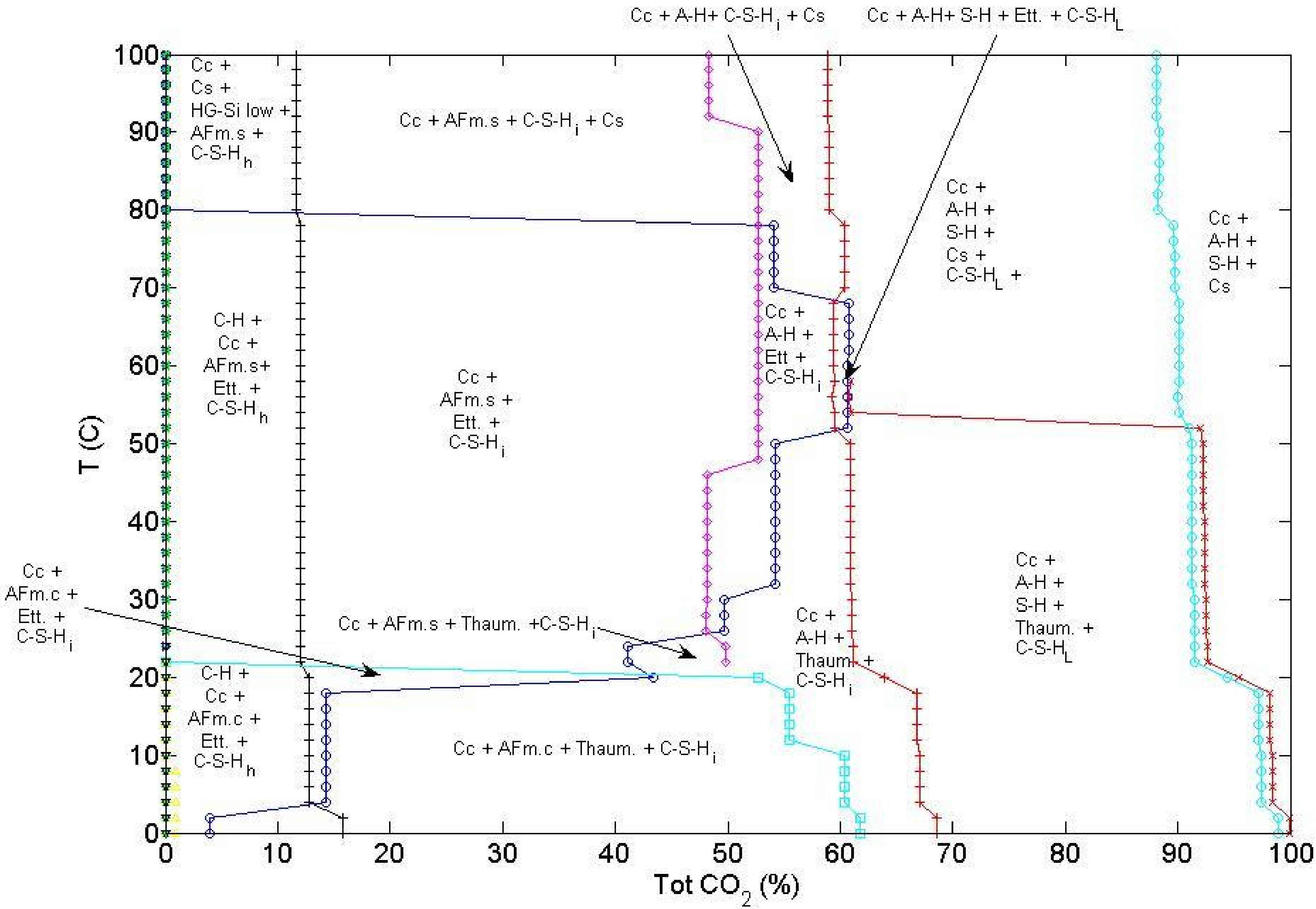
➢ T vs CO2 diagram using the Full built LogK database



➢ **Only 2 C-S-H: C-S-H_h and C-S-H_L**



➢ Calcium monosulfo aluminate: LogKf = -71.3 (instead of -72.4)



➢ C. Towards quantitative long term predictions…

Use of reactive/transport code:

HYTEC (School of Mines),

NUFT (LLNL),

FLOTRAN (LANL),

TOUGH REACT (LBNL),

….

1-Coupling of a transport code to a geochemical code:

Sequential Non-Iterative Approach

Sequential Iterative Approach

2- Transport of total concentration of a mobile chemical element (N_c-1= 9).

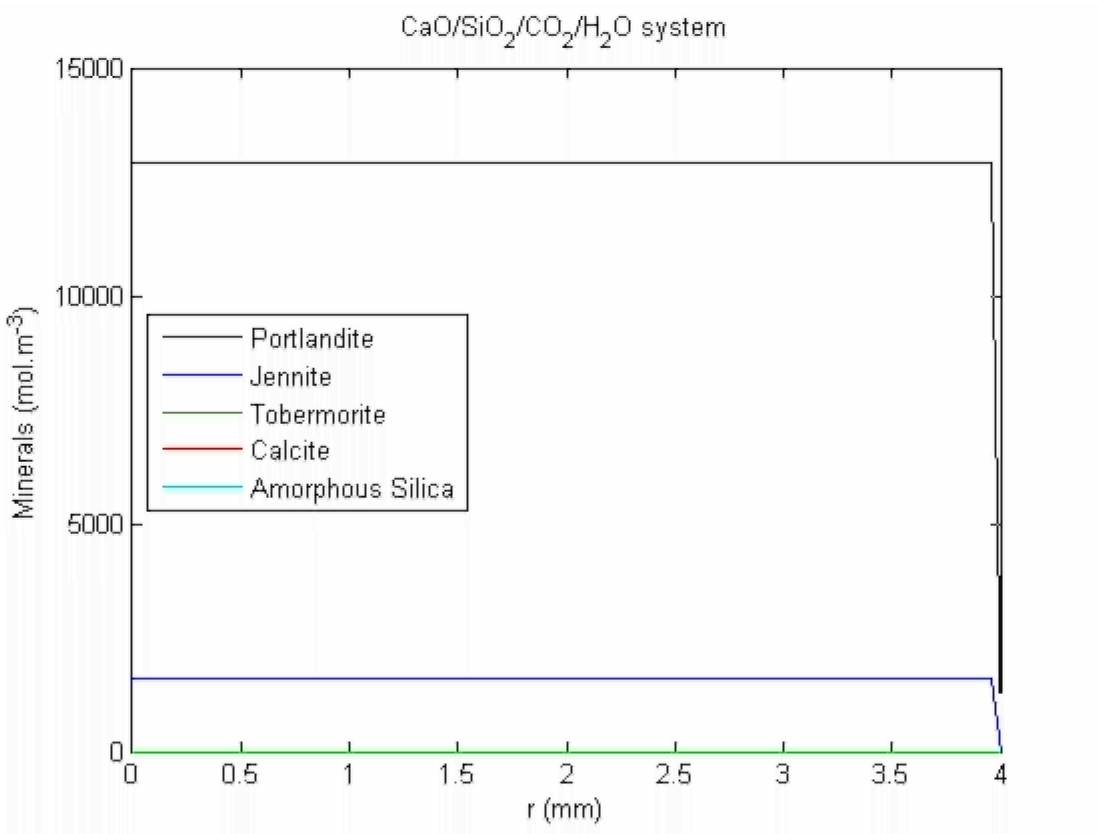
⇨ Same diffusion properties for every aqueous species

3- Main assumptions:

- Local chemical equilibrium / kinetic
- Mechanism taken into account and associated database

➢ Mineralogical profile:

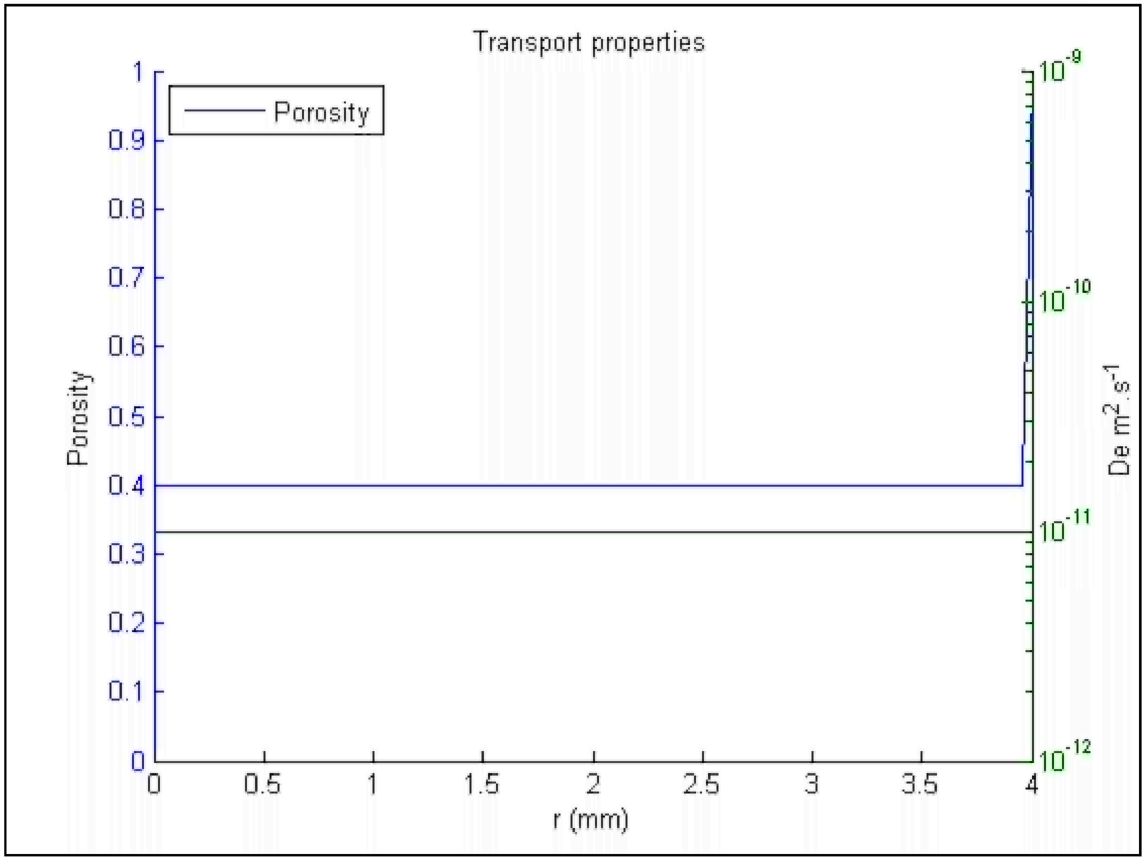
$CaO/SiO_2/CO_2/H_2O$ system



➢ Change in porosity and diffusion coefficient:

Archie's law ➔

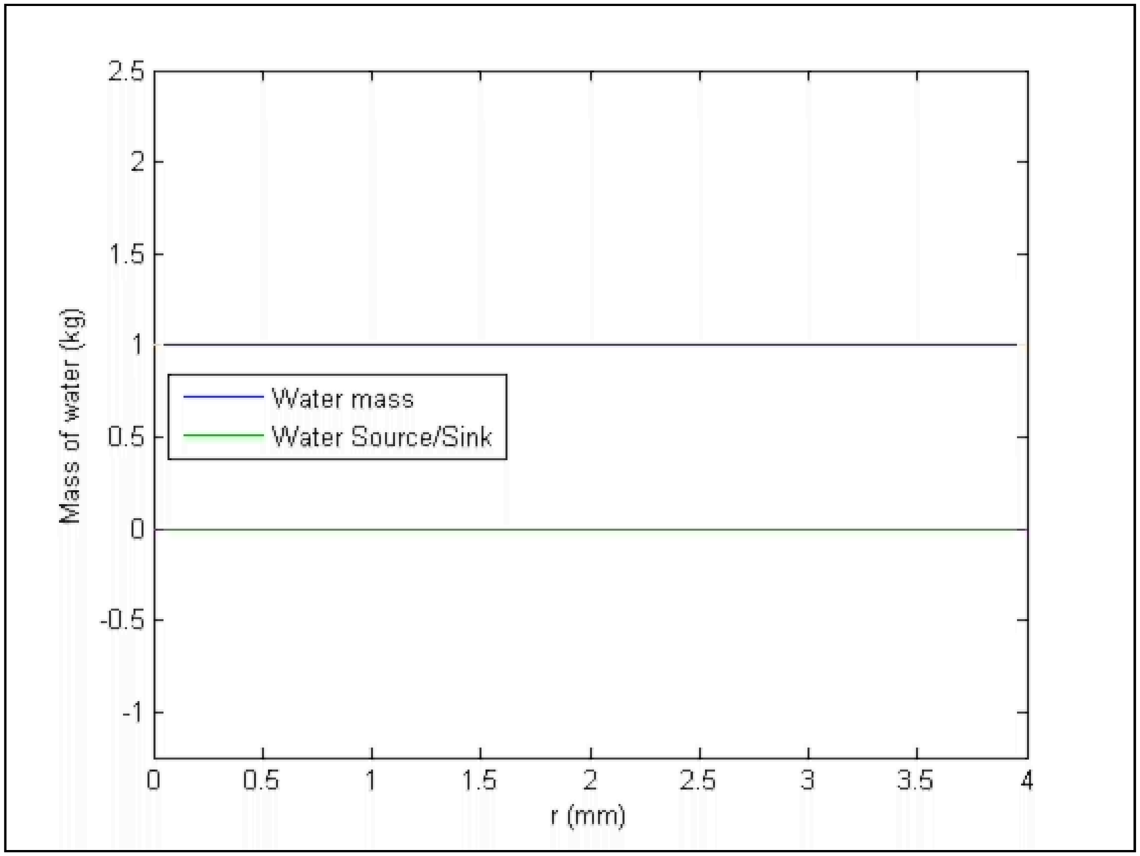
$$D_{e,t} \;=\; D_{e,t} \cdot \left(\frac{\phi_t - \phi_c}{\phi_0 - \phi_c} \right)^m \qquad , \quad m = 3.32$$



➢ **Diffusion driven advection:**

1- Water released from hydrate during their degradation

2- Change in the mean density of the paste



Conclusion

- **Thermodynamics of cement hydrates**

  - few exhaustive Dataset (Babushkin et al.)

  - scattering of standard Gibbs free energies

But - LogK = f(T) using best estimates

- **Develop interactive common database**

  - ensure internal consistency

- **Necessity of modeling solid solution of C-S-H**

- **Challenge for reactive/transport code**

  1- Modeling accurately transport properties as a function of porosity change

  ⇨ diffusivity change over order of magnitudes (10^{-12} to 10^{-9} $m^2.s^{-1}$).

  2- Quantify diffusion driven advection in fully saturated conditions